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Amplified spontaneous emission and collisional transfer from the $f^0_9(3P_0)$ ion-pair state of $I_2$

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The work presented here extends previous studies of amplified spontaneous emission (ASE) between ion-pair (charge-transfer) states of $I_2$ and shows that ASE can occur between states correlating with different states of the cation, namely, $f^0_9(3P_0)$ and $D^0_3(3P_2)$, despite the smaller transition dipole moment between them. A value of 0.34 e Å is obtained for the transition dipole under experimental conditions where the $f^0_9(3P_0) \rightarrow D^0_3(3P_2)$ ASE is eliminated. No $D^0_3(3P_0) \rightarrow f^0_9(3P_0)$ ASE transfer is observed despite the combination of favorable Franck–Condon factors and transition dipole moments. The $F^0_3(3P_0) \rightarrow f^0_9(3P_0)$ transfer is shown to be purely collisional and a propensity for transfers involving the smallest energy mismatch is observed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3098501]

I. INTRODUCTION

In most reported examples of amplified spontaneous emission (ASE) in small gas phase molecules at least one experimental parameter has to be extreme: long path lengths (1 m) for $I_2$ [Box (ab) → X(α)], where $a$ and $b$ refer to the dissociation products, $I(3P_3)$ and $I(3P_3)$, respectively] focused, high-power lasers (50 mJ/pulse) for $H$, (Ref. 2) or high pressures (>30 Torr) for CO (Ref. 3) and ND$_3$. However, in two series of experiments it has been shown that the process can be readily observed without the need for any of these extreme conditions by using optical-optical double resonance (OODR) excitation. First, Tsukiyama and co-workers$^5–8$ used the technique to study NO. ASE was observed from transitions between Rydberg states where, like its atomic analog, it occurs for states of higher principal quantum number in the far infrared. Second, ASE was observed$^{9–12}$ between three pairs of ion-pair (IP) states of $I_2$, namely, $E^0_3(3P_0) \rightarrow D^0_3(3P_2)$, $Y^0_3(3P_2) \rightarrow \beta^0_3(3P_3)$, and $f^0_9(3P_2) \rightarrow F^0_3(3P_2)$, for which there is no atomic analog. The partners in each of these pairs of states are in the same tier, i.e., they correlate with $f^0$ in the same spectroscopic state ($3P_2$ for the first two pairs and $3D_2$ for the last pair). The energy separation of these g/u pairs near their equilibrium separation is small and the associated ASE again lies in the far infrared, typically at 200–800 cm$^{-1}$.

The threshold concentration for the ASE effect is given$^{13}$ by

$$N_c = N_{i^0}N_{k^0} = 8 \pi \Delta \nu / L \Lambda^2 A_{i^0'k^0},$$

where $N_{i^0}N_{k^0}$ is the population of the upper (lower) level and $L$, $\Delta \nu$, and $\Lambda$ are the length of the active medium, the spectral width, and wavelength, respectively. $A_{i^0'k^0}$, the Einstein coefficient, is given by

$$A_{i^0'k^0} = 32 \pi^3 \mu_{i^0'k^0}^2 / 6\epsilon_0 \hbar^3$$

and the transition dipole $\mu_{i^0'k^0}$ if the Franck–Condon factor (FCF) is introduced, hence

$$N_c = \epsilon_0 \hbar \Delta \nu / 2\pi L\mu_{ab}^2.$$
also readily observed in the visible at 425 nm. For this type of transition the transition dipole is an order of magnitude smaller than for transitions between \( g/u \) pairs of IP states. The characteristic time profile of the \( E0^g_s(^3P_D) \rightarrow B0^u_s(ab) \) ASE emission has been measured by Nakano et al.\(^\text{12}\)

When several channels of ASE originating in different electronic transitions are open, the decay is a competitive process and the dominant channel may well be decided by the availability of trigger photons once the threshold population has been reached. In all cases, the trigger photon may come from spontaneous emission. However, for IP \( \rightarrow \) IP transitions in the same tier, these trigger photons may also come from black-body radiation as in NO.\(^\text{8}\) In the case of IP \( \rightarrow \) valence ASE, e.g., \( E0^g_s(^3P_D) \rightarrow B0^u_s(ab) \), the robustness of the effect under widely different experimental conditions suggested that photons in the wings of the dye laser output used in the probe step may also be responsible.

In the present paper, we investigate whether ASE, or the consequences of it, originating from transitions between IP states of opposite \( g/u \) parity in different tiers can be observed under the experimental conditions used in OODR work. The transition dipoles will be considerably smaller than between IP states in the same tier and \( \mu_{ik} \rightarrow 0 \) as the IP separation \( R \rightarrow \infty \), but very large FCFs (~1) can be found among adjacent vibrational levels in the initial and final states.

We have chosen the \( f0^g_s(^3P_0) \rightarrow D0^u_s(^3P_2) \) transition, between states in the second and first tier, for investigation. The dominant ASE transition from the \( f0^g_s(^3P_0) \) state would be expected to be its partner, the \( F0^u_s(^3P_0) \) state. However, the electronic origin of the \( f0^g_s(^3P_0) \) state lies below that of the \( F0^u_s(^3P_0) \) state and consequently each \( v_f \) level lies below the vibrational level \( v_f \) with which it has the largest FC overlap (which occurs when \( v_f \approx v_F \)) and hence ASE between them cannot take place. Evidence, in the form of \( D0^u_s(^3P_2) \rightarrow X0^g_s(aa) \) emission at 320 nm, for \( f0^g_s(^3P_0) \rightarrow D0^u_s(^3P_2) \) ASE transfer, which would occur around 1700 nm, will be presented. The trigger for ASE in this case would be spontaneously emitted photons rather than black-body radiation or laser light. The excitation and emission pathways are illustrated in Fig. 1. The potential energy curves of the \( X0^g_s(aa) \), \( B0^u_s(ab) \), \( D0^u_s(^3P_2) \), \( f0^g_s(^3P_0) \), and \( F0^u_s(^3P_0) \) states and the FCFs were calculated using the RKR1 and LEVELS programs of LeRoy.\(^\text{14,15}\) and the published molecular constants.\(^\text{16-20}\)

While ASE itself may not be of direct spectroscopic interest, its occurrence, if unsuspected, can profoundly affect collisional energy transfer studies between the vibronic states connected by ASE, transition dipole measurements between such states, and lifetime measurements. It is then important to work under non-ASE conditions and the ease with which ASE can be generated may not have been recognized in the past. We illustrate this by a measurement of the \( f0^g_s(^3P_0) \rightarrow D0^u_s(^3P_2) \) transition dipole. If, as we show, this is large enough to initiate ASE at excited state concentrations and with path lengths commonly used in OODR work, measurements of population transfer due solely to spontaneous emission without amplification must be made under controlled cell conditions.

In the course of the present work we observed \( F0^u_s(^3P_0) \rightarrow X0^g_s(aa) \) emission following excitation of the \( f0^g_s(^3P_0) \) state that indicated that the \( F0^u_s(^3P_0) \rightarrow f0^g_s(^3P_0) \) transfer was via highly selective vibrational channels. Since, in two cases, the channels involved energy changes that were slightly endothermic, this cannot be excitation transfer by ASE. The mechanism is clearly collisional energy transfer between the two states of opposite \( g/u \) parity and we present some preliminary results for this transfer.

II. EXPERIMENTAL

A XeCl excimer laser (Lambda Physik EMG 201MSC) simultaneously pumped two Lambda Physik dye lasers; an FL 2002 operating with the dye C153 and an FL 3002E operating with the dye PTP (both \( \sim 3 \) ml/pulse), provided the pump and probe photons, respectively. In all experiments known rotational levels with \( J=50 \pm 1 \) of various vibrational levels of the \( f0^g_s(^3P_0) \) state were excited. In the various excitation schemes, \( J \) was varied in order to ensure that the probe laser did not excite another rovibronic level in addition to the rovibrational level of the \( f0^g_s(^3P_0) \) state of interest. The vibrational level in the intermediate \( B0^u_s(ab) \) state was chosen so as to maximize the FCF for the probe stage.

The unfocused, counterpropagating, temporally overlapped pump and probe beams were directed through the glass sample cell that was fitted with Spectrosil quartz windows. The entrance/exit windows for the laser beams were at the Brewster angle. The cell was evacuated with a rotary backed turbo pump to a base pressure of \( 1 \times 10^{-3} \) Torr that was measured by a 10 Torr MKS Baratron gauge connected directly to the cell. The solid \( I_2 \) was held in a side arm of the cell. Unless stated otherwise, the spectra were recorded with \( I_2 \) at its vapor pressure of \( \sim 0.23 \) Torr.

The 15 cm long sample cell was positioned approximately halfway between two turning mirrors situated 4 m
apart. The pump and probe beams were aligned with two different geometries: (i) “parallel” where the beams completely overlap on both turning mirrors and (ii) “perpendicular” where the beams cross in the emission collection region at an angle of 7°, the largest angle possible with the present cell. In effect, this reduces the path length L from 15 cm to <1 cm.

The 90° emission was dispersed by a Jobin-Yvon HRS2 (f/7, 0.6 m) monochromator and monitored by a Hamamatsu R928 photomultiplier tube. In order to collect 180° emission, a quartz plate was placed at 45° relative to the laser axis, directing ~10% of the combined pump laser beam and 180° emission into the spectrometer. Dispersed emission with λ ≤ 350 nm was collected via a UG5 optical filter. While a lens was used to collect the 90° emission, the 180° emission was observed without any focusing optics.

The spectrometer slit width, i.e., the parameter that determines the resolution of the instrument remained constant throughout. The slit height was varied to ensure that the intensity of the emission gave a linear response from the photomultiplier. The output from the photomultiplier was processed by a Stanford Research SR250 gated integrator and stored on a personal computer.

Wavelength calibration of the dispersed fluorescence spectra was achieved by simultaneously recording the emission lines of a neon-filled lead hollow cathode lamp. The spectra used to determine the f0(3P0) → do(3P2) transition dipole shown were corrected for the response function of the detection system in dimensions of power per unit wavelength. None of the spectra presented in the figures have been corrected in this way.

III. RESULTS

A. f0(3P0) → do(3P2) ASE

1. f0(3P0) (v=0)

An overview of the 90° emission observed in the range 250–350 nm following excitation of (v=0) of the f0(3P0) state of I2 via an OODR path involving (u=17) of the B0u(ab) state using parallel laser beams is shown in Fig. 2(a). Vibrational progressions from four electronic transitions, together with a bound-to-free continuum from a fifth, each with a Gaussian envelope characteristic of emission from (v=0), are observed. The strongest emission between 330 and 350 nm comes from the (parallel) f0(3P0) → B0u(ab) transition. Weak (perpendicular) f0(3P0) → A1u(aa) and f0(3P0) → C1u(aa) direct emission from the initially excited state is also observed. In addition, weak D0u(3P2) → X0g(aa) and F0u(3P0) → X0g(aa) indirect emissions are also observed.

The D0u(3P2) → X0g(aa) emission must result, at least in part, as a consequence of f0(3P0) (v=0) → D0u(3P2) (v =0) ASE transfer. In an earlier paper11 we showed that the magnitude of ASE can be controlled by partial misalignment of the laser beams, i.e., by varying L in Eq. (1). Nakano et al.12 used a broadly similar approach to eliminating ASE by having the beams cross at 30°. In the present study we use beams crossing at 7° in an attempt to eliminate ASE. Emissions of the emission spectra in the range 286–327 nm recorded with parallel and 7° beams are shown in the lower and upper traces of Fig. 3(a), respectively. The spectra are normalized to the intensity of the f0(3P0) → C1u(aa) emission. The relative intensity of the D0u(3P2) → X0g(aa) emission in the spectrum recorded with 7° beams is greatly decreased, confirming that the f0(3P0) (v=0) → D0u(3P2) (v =0) transfer is predominantly by ASE when parallel beams are used.

2. f0(3P0) (v=2)

An overview of the 90° emission observed in the range 250–350 nm following excitation of (v=2) of the f0(3P0) state of I2 via an OODR path involving (u=21) of the B0u(ab) state using parallel beams is shown in Fig. 2(b). D0u(3P2) → X0g(aa) emission resulting from f0(3P0) (v =2) → D0u(3P2) (v =2) ASE transfer is observed in the range 300–330 nm.

As before, the f0(3P0) (v=2) → D0u(3P2) (v =2) ASE can be eliminated by using 7° beams [Fig. 3(b)]. In addition, in the spectra recorded using 7° beams at three different I2 pressures shown in Fig. 4(a), the intensity of the D0u(3P2) → X0g(aa) emission relative to that of the f0(3P0) (v=2) → C1u(aa) direct emission does not vary with I2 pressure. Hence, the D0u(3P2) → X0g(aa) emission cannot be due to...
state of ASE transfer is observed in the range 285–315 nm. Between 124302-4 Ridley, Lawley, and Donovan J. Chem. Phys. 130

In each panel, the lower and upper traces were recorded with parallel and 7° laser beams, respectively. The spectra are normalized to the intensity of the optical transition, the precursor of the ASE transfer. We will

\[ f_3^{1}(P_{0}) \rightarrow D_3^{1}(P_{2}) \]

collisional transfer. Therefore, it is concluded that the \( D_3^{1}(P_{2}) \rightarrow X_0^{1}(aa) \) emission observed in the 7° spectrum results purely from \( f_3^{1}(P_{0}) \) \( (v=2) \) \( \rightarrow D_3^{1}(P_{2}) \) \( (v=2) \) transfer by a spontaneous nonamplified optical transition, the precursor of the ASE transfer. We will use these experimental conditions in Sec. III to determine the \( f_3^{1}(P_{0}) \rightarrow D_3^{1}(P_{2}) \) transition dipole.

In contrast, the intensity of the \( F_0^{0}(3P_{0}) \rightarrow X_0^{0}(aa) \) emission relative to that of the \( f_0^{1}(P_{0}) \rightarrow A_{1s}(aa) \) direct emission does vary with \( I_2 \) pressure as shown in the spectra in Fig. 4(b). Therefore, it is concluded that the \( F_0^{0}(3P_{0}) \rightarrow X_0^{0}(aa) \) emission results from \( F_0^{0}(3P_{0}) \rightarrow f_0^{1}(3P_{0}) \) collisional transfer as proposed in earlier studies.\(^{21,22}\) This transfer will be discussed further in Sec. IV.

3. \( f_0^{1}(3P_{0}) \) \( (v=8) \)

An overview of the 90° emission observed in the range 235–350 nm following excitation of \( (v=8) \) of the \( f_0^{1}(3P_{0}) \) state is shown in Fig. 2. \( D_0^{0}(3P_{2}) \rightarrow X_0^{0}(aa) \) emission resulting from \( f_0^{1}(3P_{0}) \) \( (v=8) \) \( \rightarrow D_0^{0}(3P_{2}) \) \( (v=8) \) ASE transfer is observed in the range 285–315 nm. Between 315 and 330 nm the high wavelength region of the

\[ D_0^{0}(3P_{2}) \rightarrow X_0^{0}(aa) \]

emission is concealed by the low wavelength region of the \( f_0^{1}(3P_{0}) \rightarrow B_0^{0}(ab) \) emission. As before, the \( f_0^{1}(3P_{0}) \) \( (v=8) \) \( \rightarrow D_0^{0}(3P_{2}) \) \( (v=8) \) ASE can be eliminated by using 7° beams [Fig. 3(c)].

4. \( f_0^{1}(3P_{0}) \) \( \rightarrow B_0^{0}(ab) \) emission

The 90° and 180° emissions from \( (v=0) \) of the \( f_0^{1}(3P_{0}) \) state excited with parallel beams is shown in Figs. 5(b) and 5(d), respectively. The intensity distribution in the 90° spectrum reproduces the FC envelope, indicated by the stick spectrum in Fig. 5(a). In contrast, only the four most intense bands are seen in the 180° spectrum. A similar effect was observed in an earlier study on the \( E_0^{1}(3P_{3}) \) state\(^{4}\) and, as before, it is concluded that the 180° signal is predominantly directly observed ASE, whereas the 90° signal is spontaneous fluorescence.

The 180° emission excited with 7° beams is shown in Fig. 5(c). It can be seen that this vibrational distribution resembles the 90° fluorescence shown in Fig. 5(b) much more closely than the 180° ASE shown in Fig. 5(d). This indicates that in the spectrum excited with 7° beams the 180° emission is almost entirely fluorescence rather than ASE. The three spectra in Fig. 5 are normalized to the intensity of the most intense band in each spectrum. However, the absolute inten-
FIG. 5. The $f^{0}_g(3P_0)\rightarrow B^{0}_u(ab)$ emission following excitation of ($\nu=0$) of the $f^{0}_g(3P_0)$ state of I$_2$ with various geometries: (b) collected at 90° and excited with parallel beams, (c) collected at 180° and excited with 7° beams, and (d) collected at 180° and excited with parallel beams. The peaks indicated by a star contain some scattered probe laser light. A stick spectrum of the positions and raw FCFs for the $(J=50)\rightarrow(J=50)$ transitions is shown in (a). No frequency, transition dipole function or detector response function corrections have been applied to the intensities in the stick spectra.

sities of the spectra in (b) and (d) are at least an order of magnitude more intense than that in (c). Previous experiments$^9$ showed that with our experimental arrangement, for any given spontaneous fluorescence, 90° collection was approximately 30 times more efficient than 180° collection. This observation further indicates that in the spectrum excited with 7° beams the 180° emission is almost entirely spontaneous fluorescence. Hence, it is concluded that the 7° geometry is effective in greatly reducing $f^{0}_g(3P_0)\rightarrow B^{0}_u(ab)$ ASE as well as eliminating $f^{0}_g(3P_0)\rightarrow D^{0}_u(3P_2)$ ASE.

B. Measurement of the $f^{0}_g(3P_0)\rightarrow D^{0}_u(3P_2)$ transition dipole

In order to determine the $f^{0}_g(3P_0)\rightarrow D^{0}_u(3P_2)$ transition dipole, the integrated fluorescence intensities of the various emission systems from the $f^{0}_g(3P_0)$ state, namely, $f^{0}_g(3P_0)\rightarrow B^{0}_u(ab)$, $f^{0}_g(3P_0)\rightarrow A^{1}_1(aa)$, $f^{0}_g(3P_0)\rightarrow C^{1}_1(aa)$, and $f^{0}_g(3P_0)\rightarrow D^{0}_u(3P_2)$, have to be obtained. $I_{ik}$, the integrated fluorescence intensity of the transition $i\rightarrow k$ relative to the total fluorescence, is then obtained from

$$I_{ik} = S_{ik}/\Sigma_k S_{ik},$$

where $S_{ik}$, in photons s$^{-1}$, is the integrated fluorescence intensity for each electronic transition.

$S_{ik}$ values for the first three systems were measured directly but that for the fourth system had to be determined indirectly by initially measuring $S_{ik}$ for $D^{0}_u(3P_2)\rightarrow X^{0}_g(aa)$, $S_{DX}$. If the $D^{0}_u(3P_2)$ state population is created solely by $f^{0}_g(3P_0)\rightarrow D^{0}_u(3P_2)$ fluorescence without any collisional or ASE transfer, as described in Sec. I, and if the $D^{0}_u(3P_2)$ state is not collisionally quenched, $S_{DX}=S_{DX}/I_{DX}$.

In an earlier study,$^{23}$ $I_{DX}$ was reported to be 0.89.

Rewriting Eq. (2), $\mu_{ik}(R_c)$, in e A, is given by

$$\mu_{ik}(R_c)^2 = A_{w',k}\nu^2 \times 7.24 \times 10^{-6},$$

where $\nu$, in wave numbers, is the median frequency of the transition and $A_{w',k}$ is given by

$$A_{w',k} = I_{ik}/\tau_i,$$

where $\tau_i$ is the lifetime of the upper state.

$S_{ik}$ values for each electronic transition $i\rightarrow k$ were determined by first recording spectra of the various emission systems from ($\nu=0$) of the $f^{0}_g(3P_0)$ state and integrating each with respect to wavelength. The values obtained were then corrected to: (i) account for the response function of the detection system (in dimensions of power per unit wavelength) and (ii) convert to units of photons s$^{-1}$. For both corrections, a single value that applies to the wavelength centroid of the narrow emission system resulting from the low upper state vibrational level was used, e.g., 341 nm for $f^{0}_g(3P_0)\rightarrow B^{0}_u(ab)$.

There is an inherent problem associated with accurately measuring the relative integrated intensities of two emission systems that differ by two orders of magnitude. The magnitude of the fluorescence collected must be large enough for the signal-to-noise ratio to be such that an accurate integrated intensity can be measured, while ensuring that it is not too large for partial saturation of the detection system to occur for the strong emission. In order to circumvent this problem, the three weak emission systems, together with the weaker part of the $f^{0}_g(3P_0)\rightarrow B^{0}_u(ab)$ emission, namely, to ($\nu=9–11$) of the lower state, were recorded with good signal-to-noise levels and ratios of the integrated intensities determined. The percentage contribution that the ($\nu=9–11$) bands make to the total $f^{0}_g(3P_0)\rightarrow B^{0}_u(ab)$ emission was then calculated from the FCFs, corrected for the wavelength, transition dipole, and response function dependencies.

The resultant $S_{ik}$ values were used to obtain $I_{ik}$ for each system and these are presented in Table I, $A_{w',k}$ and $\mu_{ik}(R_c)$ for each transition were then obtained from Eqs. (7) and (8) using a fluorescent lifetime of 13.7 ns,$^{24}$ and these are also presented in Table I. The errors in $I_{ik}$ and $\mu_{ik}(R_c)$ for the weak emissions are estimated to be $\sim 20\%$ and $\pm 10\%$, respectively. The $I_{ik}$ values for $f^{0}_g(3P_0)\rightarrow A^{1}_1(aa)$ and $f^{0}_g(3P_0)\rightarrow C^{1}_1(aa)$ are approximately one third of those reported previously$^{23}$ for these weak transitions and replace those erroneous values.

The $S_{ik}$ value for the $f^{0}_g(3P_0)\rightarrow D^{0}_u(3P_2)$ transition was obtained by dividing the value for $D^{0}_u(3P_2)\rightarrow X^{0}_g(aa)$ by 0.89.$^{23}$ However, this value is an upper limit as it has been subsequently shown$^{10}$ that there is some $D^{0}_u(3P_2)\rightarrow 0^+_g(bb)$ emission, for which the transition dipole is unknown, that was not included in the original calculation. If a value for the
While the transition dipole $\mu_0^{(3)P_2}$ is large, the FCF is very small for $f_{00}^{(3)P_2}/H_2O^{(4)P_2}/H_1$ transitions. This, in turn, increases the value of $\mu_0^{(3)P_2}/H_2O^{(4)P_2}/H_1$, i.e., the value is fairly insensitive to the magnitude of the transition dipole for $g/u$ transitions within the same tier of IP states (~3.6 e Å). However, 0.34 e Å is just over half the magnitude of the dipole for the $E0^{(3)P_2}→0^{(3)P_2}/H_1$ and $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →B0^{(3)P_2}/H_1$ IP → valence transitions where ASE has been observed directly and this would explain why $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →D0^{(3)P_2}/H_1$ ASE can be induced under favorable experimental conditions. Had the transition dipole been determined from spectra recorded in the presence of ASE, i.e., from the spectrum recorded with parallel beams [the lower trace of Fig. 3(a)] rather than from the spectrum recorded with 7° beams [the upper trace of Fig. 3(a)], it would have been approximately three times too large.

C. $f0^{(3)P_0}→f0^{(3)P_0}$ transfer

1. ASE transfer

Expansions of the $F0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →X0^{(3)P_2}/H_1$ emission spectra in the range 255–275 nm following excitation of $(v=2)$ of the $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1$ state recorded with parallel and 7° beams are shown in the lower and upper traces of Fig. 6(a), respectively. The spectra are normalized to the intensity of the $F0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →A1_{u}(aa)$ emission (not shown). The spectra are dominated by emission from $F0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →X0^{(3)P_2}/H_1$, $g/u$ transitions are equal, this corresponds to the $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →D0^{(3)P_2}/H_1$ transition (0.13) where ASE can be induced.

Expansions of the emission spectra in the range 275–235 nm, normalized to the intensity of the $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →A1_{u}(aa)$ emission, following excitation of $(v=8)$ of the $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1$ state recorded with parallel and 7° beams, are shown in the lower and upper traces of Fig. 6(b), respectively. The spectra are dominated by emission from $F0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →X0^{(3)P_2}/H_1$. As for $(v=2)$, the relative intensity and the vibrational distribution in the $F0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →X0^{(3)P_2}/H_1$ emission in the two spectra are essentially the same indicating that there is no appreciable $F0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →f0^{(3)P_0}/H_2O^{(4)P_2}/H_1$ ASE transfer.

The absence of $F0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →F0^{(3)P_0}/H_2O^{(4)P_2}/H_1$ ASE

$$N_c \approx 1/\mu_{ab}(R_s^2 q_{v=0}^n)$$

the value of the denominator (0.026) is much smaller than that for the $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →D0^{(3)P_2}/H_1 (v=2)$ transition (0.13) where ASE can be induced.

TABLE I. Analysis of the integrated fluorescence from the $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1$ IP state. The values for the $D0^{(3)P_2}/H_1$ state were obtained by inference, assuming a certain model for the $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1$ state as described in the text.

<table>
<thead>
<tr>
<th>Lower state</th>
<th>$\lambda$/nm</th>
<th>Wave number/cm$^{-1}$</th>
<th>$I_d$</th>
<th>$A_{uv}(R_s)/10^5$ s$^{-1}$</th>
<th>$\mu_{ab}(R_s)/e$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1$\alpha$(aa)</td>
<td>282</td>
<td>35 461</td>
<td>0.003 91</td>
<td>2.85</td>
<td>0.030</td>
</tr>
<tr>
<td>C1$\alpha$(aa)</td>
<td>292</td>
<td>34 247</td>
<td>0.004 01</td>
<td>2.93</td>
<td>0.032</td>
</tr>
<tr>
<td>B0$\alpha$(ab)</td>
<td>341</td>
<td>29 326</td>
<td>0.990</td>
<td>723</td>
<td>0.63</td>
</tr>
<tr>
<td>D0$\alpha$(P2)</td>
<td>1667</td>
<td>5999</td>
<td>0.002 42</td>
<td>1.77</td>
<td>0.34</td>
</tr>
</tbody>
</table>

FIG. 6. The 90° $F0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →X0^{(3)P_2}/H_1$ emission spectra in the range 275–250 nm following excitation of (a) $(v=2)$ and (b) $(v=8)$ of the $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1$ state recorded with parallel and 7° beams. The spectra are normalized to the intensity of the $f0^{(3)P_0}/H_2O^{(4)P_2}/H_1 →A1_{u}(aa)$ emission (not shown).
transfer is surprising as \(f0^+_g(3P_0) (v=8)\) lies 72 cm\(^{-1}\) above \(F0^+_g(3P_0) (v=6)\). The FCF for this transition is larger (3.4 \(\times 10^{-5}\)) making the value of the denominator in Eq. (9), (0.44), greater than that for the \(f0^+_g(3P_0) (v=8)\rightarrow D0^+_g(3P_2) (v=8)\) transition where ASE can be achieved.

Although the critical concentration for \(F0^+_g(3P_0) \rightarrow f0^+_g(3P_0)\) ASE can probably be achieved, the absence of ASE points to the crucial role of trigger photons. The smaller FCFs for even the most favorable \(F0^+_g(3P_0) \rightarrow f0^+_g(3P_0)\), \(q_{86} =0.034, q_{20}=0.0021\) compared with \(q_{86}=0.92, q_{22}=0.97\) for the competing \(f0^+_g(3P_0) \rightarrow D0^+_g(3P_2)\) transitions, combined with the very different fluorescent wavelengths means that the Einstein coefficients, and hence the rates of spontaneous emission of trigger photons for the \(F0^+_g(3P_0) \rightarrow f0^+_g(3P_0)\) transitions are very small compared with those for the \(f0^+_g(3P_0) \rightarrow D0^+_g(3P_2)\) transitions. The only way in which an \(F0^+_g(3P_0) \rightarrow f0^+_g(3P_0)\) transition could exhibit ASE would be through efficient triggering by black-body photons, the rate of which is \(n_AF_F\), where \(n\) is the photon occupation number at \(\nu_F\). For the most favorable case of \(F(v=0) \rightarrow f(v=2)\), for which \(n_F=20\) cm\(^{-1}\), \(n\approx 10\), but \(n_AF_F\) is still only 1.1 \(\times 10^{-8}\) \(A_m\), in spite of the more favorable intralayer transition dipole.

2. Transfer by collisions with ground state \(I_2\)

As no evidence for \(F0^+_g(3P_0) \rightarrow f0^+_g(3P_0)\) ASE is observed, it is concluded that the transfer is due to collisions with \(I_2\times X0^+_g(aa)\). Stick spectra of the positions and raw FCFs for the \((J=50) \rightarrow (J=50)\) transitions of the various \(F0^+_g(3P_0) \rightarrow X0^+_g(aa)\) vibronic bands observed following excitation of \(f0^+_g(3P_0) (v=2\ and \ 8)\) using 75 \(^\circ\) beams are shown in Figs. (7a) and (7b), respectively. No frequency, transition dipole function, or detector response function corrections have been applied to the intensities in the stick spectra since in both cases an estimate of the relative concentrations of the \(F0^+_g(3P_0)\) state levels can easily be made from a narrow wavelength region at the blue end of the emission system where the component bands become resolved. Thus, we estimate the relative concentrations of \(F0^+_g(3P_0) (v=0):(v=1):(v=2)\) to be 10:1.5:1 following excitation of \(f0^+_g(3P_0) (v=2)\) and of \(F0^+_g(3P_0) (v=6):(v=7):(v=8)\) to be 1:10:2.5 following excitation of \(f0^+_g(3P_0) (v=8)\).

The propensity for \(F0^+_g(3P_0) (v=0) \rightarrow f0^+_g(3P_0) (v=0)\) [Fig. 2a)] is not surprising as the final state level lies 190 cm\(^{-1}\) above the initial level (\(\Delta E=190\) cm\(^{-1}\)), hence transfer to higher levels would involve an even greater increase in energy. The dominant transfer from \(f0^+_g(3P_0) (v=2)\) goes to \(F0^+_g(3P_0) (v=0)\), the level with the smallest energy mismatch (\(\Delta E=20\) cm\(^{-1}\)) but with a small FCF (2 \(\times 10^{-3}\)) in preference to going to \(F0^+_g(3P_0) (v=2)\), the level with the largest FCF (0.85) and an energy mismatch of \(\Delta E =170\) cm\(^{-1}\). The dominant transfer from \(f0^+_g(3P_0) (v=8)\) goes to \(F0^+_g(3P_0) (v=7)\), as before, the level with the smallest energy mismatch (\(\Delta E=20\) cm\(^{-1}\)) in preference both to \(F0^+_g(3P_0) (v=8)\), the level with the largest FCF and \(\Delta E =110\) cm\(^{-1}\), and \(F0^+_g(3P_0) (v=6)\), a transfer involving a loss of energy (\(\Delta E=70\) cm\(^{-1}\)).

Akopyan et al.\(^{25,26}\) studied the collisional transfer from

![FIG. 7. The 90° \(F0^+_g(3P_2) \rightarrow X0^+_g(aa)\) emission spectra in the range 275–250 nm following excitation of (a) \((v=2)\) and (b) \((i=8)\) of the \(F0^+_g(3P_0)\) state. The stick spectra show the positions and raw FCFs for the \((J=50) \rightarrow (J =50)\) transitions without any frequency, transition dipole function, or detector response function corrections. The relative concentrations shown are (a) \((v=0):(v=1):(v=2)\) 10:1.5:1 and (b) \((v=6):(v=7):(v=8)\) 1:10:2.5.

\((v=8)\) of the \(f0^+_g(3P_0)\) state by \(I_2\times X0^+_g(aa)\). Following excitation of \(f0^+_g(3P_0) (v=8, J=55)\) they observed the strongest emission from \(F0^+_g(3P_0) (v=6, 7, 8)\) in the approximate ratios 1:2.2:2; ratios that are significantly different to those observed in the present study, i.e., 1:10:2.5. This intriguing observation merits more extensive investigation.

IV. CONCLUSIONS

Direct \(f0^+_g(3P_0) \rightarrow B0^+_g(ab)\) ASE has been observed that can be largely suppressed by reducing the length of the active medium, i.e., by having the pump and probe beams at 7\(^{\circ}\) to each other. In addition, \(f0^+_g(3P_0) \rightarrow D0^+_g(3P_2)\) ASE from \((v=0, 2, 8)\) has been observed indirectly by collecting subsequent \(D0^+_g(3P_2) \rightarrow X0^+_g(aa)\) emission. This ASE can be totally suppressed in the same way. A value of 0.34 e Å has been obtained for the \(f0^+_g(3P_0) \rightarrow D0^+_g(3P_2)\) transition dipole using 7\(^{\circ}\) beams. The value is similar to those for the strongest IP valence transitions and explains why ASE can be induced.

No \(F0^+_g(3P_0) \rightarrow f0^+_g(3P_0)\) ASE transfer from \((v=0, 2, 8)\) has been observed, despite the combination of FCFs and transition dipoles apparently being favorable in some cases. It has been proposed that this is due to a low abundance of trigger photons for the transitions. Highly selective vibrational channels for \(F0^+_g(3P_0) \rightarrow f0^+_g(3P_0)\) collision transfer by
$I_2 X0e^+(aa)$ have been observed in which transfer from $(v = 2$ and $8)$ goes predominantly to $(v = 0$ and $7)$, respectively, showing a propensity for transfers involving the smallest energy mismatch.

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